

National Exposure Research Laboratory
Research Triangle Park, NC

Quality Assurance Project Plan ADDENDUM 1:
Non-Targeted Analyses of Per- and Polyfluoroalkyl Substances (PFAS)
for New Hampshire Department of Environmental Services (NHDES)

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**Quality Assurance Project Plan ADDENDUM 1:
Non-Targeted Analyses of Per- and Polyfluoroalkyl Substances (PFAS)
for New Hampshire Department of Environmental Services (NHDES)**

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Preface

This Addendum 1 (QAPP ID: D-EMMD-0031346-QP-1-1) is associated with the Quality Assurance Project Plan: Non-Targeted Analyses of Per- and Polyfluoroalkyl Substances (PFAS) for New Hampshire Department of Environmental Services (NHDES) (QAPP ID: D-EMMD-PHCB-015-QAPP-01 / D-EMMD-0031346-QP-1-0) and serves as the plan for analysis of additional air, air extracts & condensates, solids, dispersions, and dusts by NERL and NRMRL scientists. Sample collection will be conducted by NHDES according to their own protocols and sample analyses will be conducted by EPA.

A3. Distribution List

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A4. Project Organization

Table 1 below describes project personnel and their respective role and responsibility for this project.

Table 1. Project personnel roles and responsibilities.

Project Personnel	Role	Responsibility
John Offenberger	Principal Investigator	Overall project development
Jeff Ryan	Principal Investigator	Project development and guidance
Mark Strynar	Principal Investigator	Sample Analysis (impinger fluids, filters, extracts) & data reporting
Andrew Lindstrom	Principal Investigator	Data reporting
Theran Riedel	Principal Investigator	Sample Analysis of Canister Air
Ingrid George	Principal Investigator	Sample Analysis of Canister Air
Dennis Tabor	Chemist	Sample extractions (filters, XAD-2)
Surender Kaushik	EPA project supervision	EPA Project oversight and approval
Adam Biales	EPA project supervision	EPA Project oversight and approval
Myriam Medina-Vera	EPA project supervision	EPA Project oversight and approval
Jackie Rosati Rowe	EPA project supervision	EPA Project oversight and approval
Richard Shores	EPA project supervision	EPA Project oversight and approval
Sania W. Tong Argao	EMMD QA Manager	Advises on QA requirements, reviews and approves project QAPP and associated SOPs
Libby Nessley	AEMD QA Manager	Advises on QA requirements and associated SOPs
Timothy Buckley	EMMD Coordinator	Coordinate project discussions between EMMD, R1 and NHDES
Brian Gullett	AEMD Coordinator	Coordinate project discussions between AEMD, R1 and NHDES
Meghan F. Cassidy	Regional supervision	Assist with overall project coordination and to help lead efforts to communicate project results to NHDES and R1 constituents

A5. Problem Definition and Background

The New Hampshire Department of Environmental Services (NHDES) through US EPA Region 1 and the US EPA's Office of Research and Development (ORD) National Exposure Research Laboratory (NERL) laboratory director, requested the assistance of NERL's Exposure Methods and Measurements Division (EMMD) for the emissions sampling and analyses of long and short-chain poly- and perfluoroalkyl substances (PFAS) by high resolution mass spectrometry with an assessment of the spectral data using library searches (i.e., non-targeted analysis). The additional samples including air, air extracts & condensates, water/liquids, solids, dispersions, and dusts, will be obtained through the state of NH from one facility historically associated with commercial use of PFAS compounds. NERL enlisted ORD's National Risk Management Research Laboratory (NRMRL) Air and Energy Management Division (AEMD) to provide additional guidance and support relative to source emissions sampling and whole air analyses.

To support NHDES' request, NERL's and NRMRL's expertise is needed to overcome the technical barriers encountered by NH including:

- 1) identifying appropriate sampling approaches for comprehensive emissions sampling;
- 2) commercial laboratory analytical limitations for handling more complex sample matrices;
- 3) unknown nature of the compounds because they are proprietary, manufacturing byproducts, or degradation compounds contained in stack gases; and
- 4) lack of expertise and experience associated with advanced fluorochemistry, and fate & transport properties.

Drs. Mark Strynar, and Andrew Lindstrom are experts in the area of polyfluoroalkyl substances (PFAS) including perfluoroalkyl ether carboxylic acids (PFECAs). They have authored about 28 publications on the topic. Dr. Theran Riedel is an expert in Chemical Ionization Mass Spectrometry (CIMS), an analytical technique that is expected to be useful for analysis of selected samples from this project. Dr. Ingrid George is an expert in gas chromatography / mass spectrometry of volatile organic compounds in source emissions, an additional analytical technique that is expected to be useful for analysis of selected samples from this project. Jeff Ryan is an expert in emissions sampling and analysis of compounds and particles from source stacks, and vents. Dennis Tabor is an expert in the preparation and analysis of emissions samples. Dr. John Offenberg is an expert in tropospheric atmospheric chemistry. The specific analyses to be conducted by each analyst are described in Section A6.

The NHDES would like to use the data provided to:

- 1) better understand the multimedia environmental distribution of fluorinated compounds emitting to the air;
- 2) begin to identify what contaminant(s) need a risk assessment based on what is being measured in the environment, including emissions to air, and
- 3) begin to assess the potential for using modified stack sampling methods (e.g. Modified Method 5 -MM5) for identification, and for quantification of fluorochemical compounds.

A6. Project/Task Description

The New Hampshire Department of Environmental Services (NHDES) will coordinate the sampling of multiple matrices and sites and send the samples to the US EPA / ORD facility located in Research Triangle Park, NC. The samples include canisters containing whole air emissions, as well as the contents of Modified Method 5 (MM5) emissions sampling trains (i.e., impingers, filters, and XAD-2 traps). In addition, NHDES will send samples of dispersions, and liquid, solid or semi-solid contents of sumps, traps, and condensates. All samples will be sent to the NERL laboratory in RTP, NC for analysis.

Emissions sampling approaches will be employed to cover a large range of PFAS compound chemical properties. ORD's characterization efforts will focus on expanding the qualitative identification of as many PFAS compounds as possible from the emissions samples collected. These qualitative identifications will be made using a combination of known compound

confirmations as well as tentative identifications using high resolution mass spectral data interpretation.

Initially, ORD will evaluate adapting the existing water analysis approach to the analysis of Modified Method 5 (MM5) train emission samples and its associated sample fractions. Although ORD has existing quantitative analytical approaches that are used for quantifying select PFAS compounds in water samples, the same quantitative analytical performance cannot be assumed for air samples. To ensure the validity of the MM5 sample train method for PFAS analyses, the target compounds must be captured and recovered (solvent extracted and concentrated) to a known extent. Without knowing the quantitative performance of these steps, it is not possible to provide quantitative data of known and acceptable quality, limiting reported results to qualitative determinations.

ORD will also be using the MM5 samples collected for EPA for methods development purposes. These samples will make it possible to begin to assess the performance of PFAS sampling capture and recovery as well as PFAS mobility within the MM5 sampling train. This will be accomplished by spiking PFAS surrogate compounds on the MM5 train's XAD-2 sorbent trap prior to sampling. The PFAS surrogate compounds that will be spiked are limited in number and it is unknown how well they will represent the actual PFAS compounds present. Without this one-to-one representation of PFAS surrogate and target compounds, it will not be possible to report PFAS emissions quantitatively.

ORD will also investigate the applicability of volatile compound sampling and analysis techniques to PFAS sampling and analysis. Whole air samples collected in SUMMA canisters is the initial approach selected for this investigation. The SUMMA canister approach is not intended for emissions sources and is being adapted from an ambient method. The ability to provide quantitative data of known and acceptable quality from the initial SUMMA sampling and analysis procedures is not possible for many of the reasons described above and for additional reasons. A major concern is the amount of moisture present in emission sources sampled and the potential for moisture to condense within the canisters after sampling. Many of the PFAS compounds of potential interest are water soluble. With moisture present in the canisters, the potential for PFAS compound reactivity/loss is significantly enhanced. Moreover, very few, if any, PFAS analytical gas standards are available at this time. Gas standards are needed to not only empirically investigate their behavior in the SUMMA canisters, PFAS analytical standards are needed to establish proper analytical conditions and confirm PFAS compound identities. As a result, any PFAS compound identifications will likely be limited to only mass spectral interpretations. It will not be possible to report volatile PFAS emissions quantitatively.

Dennis Tabor will perform solvent extractions and concentrations of the solid MM5 train components (filters, XAD-2 traps) for subsequent NERL analyses.

Mark Strynar will perform non-targeted analysis on all MM5 extracts and additional samples received (i.e., not whole air SUMMA canister samples) including impinger fluids & extracts, XAD-2 & filter extracts, and condensate/fluid extracts.

Theran Riedel will perform non-targeted analysis on whole air (SUMMA canister) by Time of Flight-CIMS (ToF-CIMS).

Ingrid George will perform non-targeted analysis on whole air (SUMMA canister) by GC-MS &/or GC-ToF-MS.

The NERL, EPA Region 1 and NHDES will meet bi-weekly to discuss logistics and any adjustments needed. EPA/ORD will send an e-mail when samples have been received, and report progress on the weekly meetings.

The estimated number of samples are four sets each of triplicate SUMMA canisters of whole air and four sets of MM5 stack sampling comprised of Filter/ XAD / triple impinger / filter components, as well as sampling train rinses. The specific sampling procedures are determined by NHDES.

US EPA / ORD/ NERL and NRMRL will follow their respective protocols and QA procedures as outlined in this QA Project Plan.

For this study, NHDES will send samples to EPA NERL after 23 April 2018 depending upon final sampling schedule arranged through NHDES. This work is an addendum to prior work (outlined in QAPP D-EMMD-0031346-QP-1-0), to include stack gasses, and associated samples (filters, fluids, extracts). The project timeline is shown in Table 2.

Table 2. Project timeline

Activity/Task	FY-18			FY-19
	Q2	Q3	Q4	Q1
Exploratory analysis and method work	X			
Develop and Finalize QAPP	X			
Field Sample Collection		X		
Non-targeted sample analysis		X		
Non-targeted data analysis and reporting		X	X	X

A7. Quality Objectives and Criteria for Measurement Data

The quality objectives of this project plan include:

- 1) Analyze all MM5, whole air, water and dispersion samples received from the NHDES sampling events;
- 2) Report to US EPA Region 1 the tentative identifications of PFAS compounds by best effort methodologies using available information, chromatographic retention times, and peak area counts (arbitrary units);
- 3) Assessment of the qualitative distribution of PFAS compounds between whole air gas, filter, sorbent, and impinger samples to gain a better understanding of the application of conventional organic sampling and analysis methods to PFAS compounds.

Blank samples (trip blanks, method blanks and solvent/gas blanks, where appropriate) will be analyzed to determine if they are free of analytes to evaluate any field or laboratory contamination that may exist. These process-blank detections are handled as described below in Section B5.

A8. Special Training/Certifications

No specific training is required for this project, but the analysts shall have completed all site specific health and safety training requirements that are applicable and be competent in the operations of the analytical instrumentation being used. Records of this training are maintained by the SHEM office or by individual researchers, respectively. This document assumes laboratory personnel will have a thorough working knowledge of basic laboratory skills, reagents, and instrumentation. Any standard operating procedures (SOPs) utilized are designed to guide a competent laboratory worker in the analysis of per- and polyfluorinated compounds and it is not intended to instruct individuals on the basic aspects of analytical chemistry.

A9. Documents and Records

Planning Documents

This QAPP is the planning document for this study. Additional documentation will be maintained in laboratory record notebooks, chain of custody (CoC) forms, and the study file.

Tracking Documents

Drs. John Offenberger and Mark Strynar (RTP) will retain copies of the sampling data logs, the field sample tracking forms, and the laboratory records describing the preparation and deployment of field quality control (QC) samples.

The CoC forms will accompany the samples shipped by NHDES to the EPA PFAS analysis laboratory and these forms will be retained by EPA after analysis. This information will be maintained in a dedicated bound EPA laboratory notebook specific for this project or a 3-ring binder. All analysts will maintain sample preparation records and analysis logs. The study file will also contain the records of QA issues, amendments to plans and SOPs, audit reports, and corrective action reports. QA records, such as audit reports, corrective action reports, etc., will be maintained by the EPA PIs. Finally, John Offenberger (RTP) and Mark Strynar (RTP) will maintain the study file documentation together with all associated final reports. All records will be maintained according to EPA specifications.

The Laboratory Research Notebooks (LRBs) are where records of the extraction and preparation of samples for analysis, the preparation of sampling containers (when appropriate), and the preparation of standard solutions for spiking, and calibration are documented. Methods and reagents used are recorded and appropriate SOPs used for analysis are also cited.

The Sample Analyses records are the instrument logs that document the analyses of samples, and contain records of specific instrument conditions, and date and time of sample data acquisition. Additional information or details on sample analyses may be documented in LRBs.

B. DATA GENERATION AND ACQUISITION

B1. Experimental Design

NHDES has developed a test matrix as noted in their “Stack Test Plan: Saint Gobain Performance Plastics Corporation, Merrimack, New Hampshire” sampling plan (developed by Barr Engineering Co. (Minneapolis, MN), revised April 2, 2018) that identifies the samples to be collected to investigate the occurrence of PFAS in various sample types that are important to their study. The NERL and NRMRL PFAS researchers provided guidance and advice to help NHDES craft the experimental design and appropriate sampling approaches. Discussions on needed QA elements were held by NHDES and the EPA research team and considered when finalizing the study design.

B2. Sampling Methods

The NHDES developed the sampling protocol used to collect the samples. NHDES’ Quality Assurance Project Plan (QAPP) includes the procedures for sampling for PFAS starting on page 246 of *Master Quality Assurance Project Plan of the Hazardous Waste Remediation Bureau, Waste Management Division, New Hampshire Department of Environmental Services, November 2012, EQA RFA#13027*.

The following samples will be collected by NHDES using the procedures cited in the NHDES QAPP:

- 1) Triplicate Modified Method 5 Train samples, which include inlet filter, XAD-2 sorbent, multiple impingers, post-impinger filter and rinse fractions, will be collected from three stacks at the Saint-Gobain facility. These will be performed one time for each stack with the addition of a further sampling after a test control device (e.g. wetted wall cyclone) is employed, which is to be tested by the facility operator. A total of seven samples is anticipated to be generated during each test (Front Filter, XAD-2 trap, 3 x impingers, Final filter, & rinse). The XAD-2 trap of each sampling train will be spiked prior to sampling with a known quantity of isotopically labelled compounds to assess compound mobility and recovery in the MM5 sampling trains as configured.
- 2) Whole air samples will be collected from stacks at Saint-Gobain. Triplicate samples of whole air will be collected into provided, pre-cleaned, pre-evacuated SUMMA canisters as follows:

Three samples from the “MA Tower” at Saint-Gobain.

NOTE: The “MA Tower” has been in operation at Saint-Gobain since 1994.

Three samples from the “MS Tower” at Saint-Gobain.

NOTE: The “MS Tower” has been in operation at Saint-Gobain since 2002.

Three samples from the “QX Tower” at Saint-Gobain both pre- and post-control device implementation.

NOTE: The “QX Tower” has been in operation at Saint-Gobain since 1989.

The QX tower will be sampled both before and after (i.e. pre- and post-) an operator specified control device, simultaneously.

Up to four (4) Silcosteel SUMMA canisters, including one per each of the above tower configurations, plus up to three (3) ambient / process inlet samples according to availability and conditions as determined during sampling.

- 3) Sump contents, scrubber make-up water sample, control device solids, if recoverable, char, dip pan formulation sample for each test run, and raw dispersions & condensate samples will be provided by NHDES, as available during the testing period(s).

EPA will analyze samples received through the chain of custody according to established protocols and procedures as described in Section B4.

Overview of approximate sample count is as follows:

MM5:

MM5 samplers:	3 trains per tower x 7 samples per train x 4 towers = 84 samples
Reagent blanks:	1 train x 7 samples per train x 1 tower = 7 samples
Field biased blank train:	1 train x 7 samples per train x 1 tower = 7 samples
Scrubber make-up water:	1 water sample = 1 water sample
Scrubber sump water:	3 water samples per tower x 1 tower = 3 water samples
Control device solids, if recoverable:	up to 3 = 3 Control Device Solids Samples
Char	3 towers x 1 sample per tower = 3 Char samples

Total MM5 Samples: 108 of various matrices

SUMMA:

3 samples per tower x 4 towers = 12 canisters
SUMMA Trip Blanks = 3 canisters
Silcosteel test canisters = 4 canisters
Ambient (i.e. inlet process air) = 3 canisters

Total SUMMA canister samples to consist of:

Pre-deployment and Post-deployment analysis* of:

12 samples + 4 test Silcosteel canisters + 3 Trip Blanks + 3 ambient / process inlet
 = 2 x 22
 = 44 total analyses

* Each canister will be analyzed pre-deployment as well as post-deployment so that any detected analytes can be identified as being present in the pre-deployment canister.

B3. Sample Handling and Chain of Custody

The NHDES will provide their chain of custody (CoC) form when shipping samples to EPA and EPA will receive samples as shipped. The EPA researcher will sign the chain of custody, and keep a copy for record. Chain of custody forms will be shipped with samples and include information such as collected by name/date, shipped by name/date, and received by name/date plus any additional sampling information necessary to document sampling time, date, duration, location and special comments (e.g., sample leak). Upon receipt at the laboratory, the sample custodian will check the contents of each shipping container for sample container breakage, and will verify that contents match the shipping lists. After logging in each sample, and signing CoC forms, the samples will be transferred to the appropriate storage facility.

SUMMA canisters received from NHDES are stored at laboratory room temperature prior to analysis.

Extracts (impinger, filter, XAD, sampling train, rinse, and corresponding extracts, etc.) are stored in a refrigerator/freezer at least less than 4°C, and no holding times are applicable to the samples.

The sample IDs are defined by the field collectors. Laboratory staff will use these assigned sample IDs and will not assign new sample identification numbers.

B4. Analytical Methods

The methods listed below summarize the sample analysis methods and the associated SOPs or manuals to be followed for sample analysis for MM5 extracts and whole air samples.

B4.1 Analysis of MM5 extracts (RTP, NC)

The analytical procedures used for this project in RTP are detailed in the following SOPs and EPA Test Methods:

- D-EMMD-PHCB-062-SOP-01: *Method for Extraction and Analysis of Perfluoroethercarboxylic acids (PFECAs) from Surface Water, Well Water and Waste Water by Ultra-High Performance Liquid Chromatography (UPLC)-Tandem Mass Spectrometry (MS/MS)*
- D-EMMD-ECB-010-SOP-01: *Exhaustive Extraction of Charged Per- and Polyfluorinated Alkyl Substances (PFASs) from Contaminated Soil & Sediment Samples with Ion-Pairing Cleanup*
- D-EMMD-ECB-011-SOP-01: *Exhaustive Extraction of Soil-Fluorotelomer Polymer Microcosms for Fluorotelomer and Perfluorinated Monomer Compounds*

- D-EMMD-PHCB-043-SOP-03: *Improved Method for Extraction and Analysis of Perfluorinated Compounds (PFCs) from Surface Waters and Well Water by Ultra-High Performance Liquid Chromatography (UPLC)-Tandem Mass Spectrometry (MS/MS)*
- D-EMMD-PHCB-034-SOP-01: *Analytical method for non-targeted and suspect screening in environmental and biological samples using Time of Flight Mass Spectrometry (TOFMS)*
- SW-846 Test Method 3542: *Extraction of Semivolatile Analytes Collected Using SW-846 Test Method 0010 (Modified Method 5 Sampling Train)*
- For non-targeted extraction and LC-MS analysis of the dispersions, waters, solids, sump contents and similar samples, existing methods as outlined in peer-reviewed journal articles and the above referenced SOPS will be used as a basis from which to start. Established methods are being developed, and the resulting methods used to extract and analyze the dispersion samples will be documented in a research notebook.

Non-targeted LC/MS analysis will be conducted on a liquid chromatograph coupled to a mass spectrometer. All LC-MS spectrometers will be tuned and calibrated using perfluorotributylamine (PFTBA), according to the manufacturer's instructions, before each sample set. Sample extracts will be analyzed under full-scan (m/z 50-950) conditions, or the scan range appropriate for the respective instrument. Instrument parameters that are analyte-specific will be recorded in the instrument log book and laboratory records / notebook of PI (or approved user). Method development and methods deemed appropriate for non-targeted analysis will be recorded by the PI. Preliminary identification of compounds will be completed by recording the m/z values of peaks of interest, and compared to mass spectral libraries and/or in house, putative identifications. Chromatographic retention times and 'area under the curve' will be reported for each tentatively identified compound. No internal standard masses (i.e. 'mass added'), nor peak areas will be reported, even if added to these samples.

- For quantification of spike recoveries (to be expressed as percent recovery of mass introduced), targeted LC/MS analysis will be conducted using a liquid chromatograph coupled with a mass spectrometer. The LC-MS spectrometer(s) will be tuned and calibrated using perfluorotributylamine (PFTBA), according to the manufacturer's instructions, before each sample set. Instrument parameters that are analyte-specific will be recorded in the instrument log book and laboratory notebook of PI (or approved user). Chromatographic retention times and percent of the total mass of compound applied in the spike will be reported for each spike recovery compound for each of the seven fractions in each MM5 sampling train. The average and standard deviation of recovery for each compound across the triplicate sampling for each sample fraction (e.g. XAD, first impinge, final filter, etc.) will be reported for each tower as well as for each blank. The list of compounds, and the anticipated mass to be added to each XAD are included in **Appendix A**.

- Non-targeted GC-MS analysis of liquid samples, if received, will be conducted on a gas chromatograph coupled to a mass spectrometer or an atomic emission detector (AED) for Fluorine compounds. All GC-MS spectrometers will be tuned and calibrated using perfluorotributylamine (PFTBA), according to the manufacturer's instructions, before each sample set. Instrument parameters that are analyte-specific will be recorded in the instrument log book and laboratory notebook of PI (or approved user). Method development and methods deemed appropriate for non-targeted analysis will be recorded in the laboratory notebook of the PI. Preliminary identification of compounds will be completed by recording the m/z values of peaks of interest, compared to in house, putative identification databases. Chromatographic retention times and 'area under the curve' will be reported for each tentatively identified compound. No internal standard masses (i.e. 'mass added'), nor peak areas will be reported even if added to these samples.

B4.2 Analysis of whole air samples (RTP,NC)

The analytical procedures used for this project are detailed in the following SOPs and methods:

- D-EMMD-AQB-013-SOP-01: *Operation of the Aerodyne/Tofwerk Chemical Ionization Mass Spectrometer*
- EPA/625/R-96/010b: *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air Second Edition Compendium Method TO-15 Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS)*
- ECAB-144: *Standard Operating Procedure for Determination of Volatile Organic Compounds in Whole Air Samples Collected in Canisters Using the Agilent 6890/5973N GC-MSD*
- ECAB-133: *Standard Operating Procedure for Cleaning Air Sampling Canisters with the Entech 3100A Canister Cleaner*
- UPLC-MS/MS method described in Rankin et al. (2016): *A North American and global survey of perfluoroalkyl substances in surface soils: Distribution patterns and mode of occurrence.*
- For non-targeted extraction and GC-MS analysis of the dispersion samples, existing methods as outlined in peer-reviewed journal articles may be used as a basis from which to start. Methods are being developed, and the resulting methods used to extract and analyze the samples will be documented in a research notebook. Whole air will be analyzed under full-scan (e.g. m/z 50-950 or the instrument specific full scan range as applicable), electron ionization-MS conditions.
- Non-targeted chemical ionization mass spectrometry (CIMS) analysis will be conducted on an Aerodyne CIMS high resolution mass spectrometer. The mass spectrometer will be tuned and calibrated using perfluorotributylamine (PFTBA), according to the manufacturer's instructions, before each sample set. Whole air will be analyzed under full-

scan (e.g. m/z 50-950), chemical ionization (I-) -MS conditions. Instrument parameters that are analyte-specific will be recorded in the instrument log book and laboratory notebook of PI (or approved user). Method development and methods deemed appropriate for non-targeted analysis will be recorded in the laboratory notebook of the PI. Preliminary identification of compounds will be completed by recording the m/z values of peaks of interest, compared to in house, putative identification database. No internal standard masses (i.e. 'mass added'), nor peak areas will be reported even if added to these samples.

- Non-targeted GC-MS analysis will be conducted on a gas chromatograph coupled to a quadrupole and/or time-of-flight mass spectrometer. Both GC-MSs will be tuned and calibrated using perfluorotributylamine (PFTBA), according to the manufacturer's instructions, before each sample set. Whole air will be analyzed under full-scan (e.g. m/z 50-950 or the instrument specific full scan range as applicable), electron ionization-MS conditions. Instrument parameters that are analyte-specific will be recorded in the instrument log book and laboratory notebook of PI (or approved user). Method development and methods deemed appropriate for non-targeted analysis will be recorded in the laboratory notebook of the PI. Preliminary identification of compounds will be completed by recording the m/z values of peaks of interest, compared to in house, putative identification databases. Chromatographic retention times and 'area under the curve' will be reported for each tentatively identified compound. No internal standard masses (i.e. 'mass added'), nor peak areas will be reported even if added to these samples.

B5. Quality Control

For non-targeted analysis, instrument blanks will be analyzed prior to the start of each sample set and periodically, as deemed necessary by the PI, during sample analysis. Due to the unknown nature of the compounds of interest, commercially available chemical standards may not be currently unavailable, and a surrogate mix of compounds (e.g., telomer alcohols and perfluorinated esters) can be analyzed in lieu of internal standards during analysis. Details of the surrogate mix of compounds used will be recoded in laboratory notebooks of the PI.

To ensure that supplies and consumable materials remain free of potential contaminants, process blanks including solvent blanks, matrix blanks, and trip or field blanks, as appropriate, will be analyzed with every analytical batch run in this evaluation. Results from these analyses must show that all analytes are nonconsequential. If any of these analyses yield target analyte concentrations that are of concern, the results of the entire batch will be flagged and a systematic evaluation of the materials used in the entire process will be conducted until the source of the contamination is found. Once the contaminated material has been identified, it will be replaced with a new batch or lot that has been tested to be free from contamination and the entire batch will be rerun.

Quality control criteria are discussed in further detail in the SOPs referenced in this document. Please refer to these specific procedures for additional details about QC for each procedure.

Sample values will be reported as “blank corrected”, as appropriate for each analysis method.

B6/B7. Instrument/Equipment Calibration, Testing, Inspection, Maintenance

The RTP MS analytical systems are tuned by the manufacturer annually during regularly scheduled preventive maintenance service, or more frequently if conditions warrant, as outlined in the appropriate SOPs. Systems are manually tuned by the operator to ensure ion intensities, relative ion abundances, mass resolution, and ion peak shape are within manufacturer’s specifications. Data on tune performance parameters is available in the instrument log files.

B8. Inspection/Acceptance of Supplies and Consumables

All supplies and consumable materials, such as solvents, reagents, labware, extraction cartridges, and other materials used in these analyses will be subjected to continuous testing as part of the RTP laboratory’s research for the past 5 years. Only materials that have been found to be reliably free from PFAS contamination will be used.

For the whole air samples, materials will be used that are as free from contamination to the extent feasible; however, the novelty of the analytical approach, may result in residual analyte. This will be monitored through the preparation and analysis of process blanks as described in Section B5.

B9. Non-direct Measurements

No secondary/existing data will be used for this project. As such this section is Not Applicable.

B10. Data Management

The data files are the electronic versions of these data. The electronic version of data is calculated by the instrument software and then exported to Excel. The file path(s) for where electronic data is stored will be documented in laboratory notebooks. Raw data (including electronic data on individual PC hard drives and group shared drives) will be backed up to a network or external hard drive. All data generated will be maintained Drs. Mark J. Strynar and John Offenbergs until completion of the project. Upon completion, data will be stored in accordance with EPA’s record management policy. All instrument data will be backed up to network drives routinely and will be archived along with other supporting data and relative correspondence at the completion of the study. Printed data will be referenced in laboratory notebooks, signed and dated in accordance with the Office of Research & Development’s Policy and Procedure Manual Section 13.02 on Paper Laboratory Records. The laboratory notebook will be the record for any procedure conducted in the laboratory and will provide the objective, procedure details, data references and discussion for project development. Data will be recorded from these experiments as observed. Any standard, solution, or sample made during these investigations will be marked with a reference number and/or will be traceable to a specific entry in the lab notebook. The laboratory notebooks

are the property of the EPA and will be stored in accordance with EPA's record management policy.

When shipping samples from NHDES to the RTP laboratory, NHDES will include the CoC sheets for each sample contained within the shipment. The CoC sheets will be stored in the PI's office along with other project records.

C. ASSESSMENTS AND OVERSIGHT

C1. Assessments and Response Actions

Data audits will be a random check of electronic and hand-entered data conducted by the EPA EMMD QA Manager (QAM), AEMD QA Manager or appropriate designees. These audits will focus on review of data transcription, calculation, and reporting. The EMMD or AEMD QAM will report to the researcher any findings requiring corrective action. Any findings and corrective measures will be noted in the file and discussed in the final report.

Internal quality control measures described in this QAPP, implemented by the technical staff and monitored by the EPA PIs, will give information on data quality on a day-to-day basis. A secondary reviewer will be designated to QA audit the data quality prior to EMMD/AEMD QAM data audit. The responsibility for interpreting the results of these checks and resolving any potential problems is shared between the technical staff and EPA PIs. In addition, the NHDES field and technical staff will report any problems that could potentially affect the data quality to the EPA PIs. The EPA staff will also be responsible for identifying problems that could affect data quality or the ability to use the data upon receipt of the samples and during the analyses. Any problems that are identified will be addressed by taking actions to control the problem, identify a solution to the problem, and ameliorate losses and correct data, where possible. All of the actions taken by the EPA PIs to correct issues will be documented in research notebooks as part of the project records.

Technical systems audit(s) (TSAs) or surveillance audit(s) will be conducted by the EMMD and/or AEMD QAM or designees to assess implementation of this QAPP. Any findings will be reported to the respective EPA PIs and corrective actions will be implemented to address those findings. Ideally, the quality control measures regulating the operation of each work area will be sufficient to maintain acceptable performance and data quality. However, in the event that a study component is not operating within the limits of acceptability, as determined by a QA assessment, a formal account of the matter must be documented by the PI as part of the project records.

The report should contain the following information:

- Description and duration of problem
- Probable cause and resolution of problem
- Statement describing data affected by problem
- Feasibility of repeating work activity and/or generating new data.

No further work may be performed until the problem has been satisfactorily resolved, and the PIs, after consult with the QA Manager as needed, has acknowledged approval to continue work.

C2. Reports to Management

The NHDES, EPA R1 and EMMD staff will meet bi-weekly, to discuss the progress of the project. The EMMD Division Director will be responsible for transmitting data results to US EPA's Region 1. These reports will be provided on a timeline agreed upon by all parties.

Results of any QA audits will be reported as part of the final report. This section will summarize any errors, deficiencies, or deviations from the QA documentation that may, or may not, have an impact on the data.

D. DATA VALIDATION AND USABILITY

D1/D2. Data Review, Verification, and Validation/Verification and Validation Methods

The data will undergo QA review by a secondary reviewer that would check for completeness, calculations, and transcription errors before delivering the data to US EPA Region 1. The data will be reported with appropriate data quality flags, as needed.

Field Sample Data Review

Not applicable as EPA staff will only be conducting sample analyses of field samples collected by NHDES. CoCs will be reviewed upon receipt of samples for any discrepancies as described in Section B3. Noted discrepancies will be documented either on the chain of custody or in the research notebook.

Data Reduction

Not applicable as this work, as described herein is non-quantitative.

Data Verification

The goal of data verification is to ensure that complete and accurate analytical information is available for all samples analyzed by the laboratory. Data verification begins during and after the period of analysis, and data entry into the Excel spreadsheet. The key personnel of the analytical team will perform the first level of review, ensuring that all data have been verified. The

mechanisms used for all data transcriptions and transmissions will be reviewed, and a random subset of all transcriptions checked.

Once the chemical measurement data have been exported into a spreadsheet (e.g. Excel), the following QA/QC checks to verify the data will be carried out:

- Sample ID checks to verify that all Sample IDs with reported data are valid Sample IDs, i.e., they were logged in as received from NHDES,
- Missing data checks to verify that all Sample IDs received from the field either had a full set of analytical data reported or were disqualified, as documented in the CoC data or in research notebooks,
- Duplicate data checks, to verify that the same analytical data were not imported into the Excel spreadsheet twice for a given sample,
- Out-of-range checks, to verify that all data for data fields limited to a code set did not violate that code set.

Data quality flags will be assigned to each chemical measurement record as needed to identify the quality and usability of the record. Data quality flags will be assigned as documented in each report, if necessary.

Data Validation

In order to non-quantitatively identify an analyte, a minimum signal to noise (S/N) ratio for any ratio (e.g., sample to blank, sample to instrumental noise) will be initially defined as 10:1 and may be adjusted as appropriate by the analyst. The minimum S/N ratio ultimately applied will be recorded in a research notebook.

The validation of the data will be encompassed in the results of the QC samples in each shipment of sample unknowns since these QC samples will reflect all the sample preparation, shipping, storage, and handling of actual field samples. For laboratory and field blanks, if the background level for a given target analyte is unacceptably high (i.e., S/N is greater than 10:1), the target analyte results for all samples affected by this background will be flagged. The recoveries of analytes in these field samples will be a reflection of recovery of analytes throughout the entire process. In addition, the recovery of the IS compounds will demonstrate the method performance on a sample by sample basis. Since the ISs are the labeled version of a representative analyte of each class, the IS recoveries may be used to effectively assess losses during analytical procedures on a sample by sample basis.

Verification and Validation Methods

In the laboratory, the data will be verified and checked at several levels. The instrument operator will generate complete a first pass assessment of accuracy of identification of analytes in samples. This will be done on-screen using an automated procedure, when possible, where the system pages

through the data for identification of each analyte in each sample. If adjustments are needed, this will be done manually by the analyst. Electronic output will include a copy of the method, a copy of each calibration curve with equation and fit printed, run list, and a summary of the quantitation for each analyte. As noted above, the electronic files will be stored on the instrument computer and backed up routinely.

The technical reviewer will review data for accuracy in identification and quantification. This reviewer will monitor retention time, mass transition, and qualifier ion ratios.

The LC-MS/MS analytical data for samples are preprocessed, and initially reviewed using spreadsheet software; this is a three-step process which can be described as follows:

- 1) The LC-MS/MS summary data are electronically transferred into an Excel spreadsheet or exported as a delimited text file that can be read in Excel. This consists of the analysis date, the sample identification number and classification (e.g., blank, QC, calibration, unknown), target analyte names, analyte and internal standard (IS) peak area counts, analyte/IS peak area ratios, quantitation ion/qualifier ion ratio, and concentration of analyte in ng/L. The first reviewer assures that this electronic transfer has been made accurately and completely.
- 2) The first reviewer hand-enters into the spreadsheet any ancillary analytical data required. Any hand-entered data will be checked by a second analyst. The spreadsheet functions as a user-friendly interface for data entry and also imposes uniformity on the reported data. For the samples, the spreadsheet requests data values in specific units that have a uniform accuracy, i.e., number of significant digits. The straight-forward design of the spreadsheet also permits all the data from any given analytical run to be reviewed by the task leaders without requiring them to invest time learning new software.
- 3) The final, tentative analyte identifications are reported as a tentatively identified compound (name), or empirical formula, along with corresponding retention time (where appropriate) and volume/mass/pressure of sample used in the analysis.

Validation of the data will be conducted by evaluating the S/N ratios and ensuring they fall within the acceptance criteria mentioned above (i.e., at least 10:1). Results that fall outside acceptance criteria will be flagged.

Percent recoveries will be calculated by the following:

$$(\text{Recovered Mass}/\text{Spiked Mass}) * 100 = \text{Percent recovery}$$

D3. Analysis and Reconciliation with User Requirements

The EPA RTP labs will summarize the results of the chemical analyses of the samples in a final report with data flags (as needed) for US EPA Region 1 that will provide information to determine data quality and tentatively identified analytes found in the samples along with peak areas. In

addition, reporting of percent recoveries (and standard deviations) of each compound spiked onto the XAD of the MM5 sampling trains will be reported.

E. References

Mei Sun, Elisa Arevalo, Mark Strynar, Andrew Lindstrom, Michael Richardson, Ben Kearns, Adam Pickett, Chris Smith, and Detlef R. U. Knappe; "*Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina.*" *Environmental Science & Technology Letters* 2016 3 (12), 415-419 DOI: 10.1021/acs.estlett.6b00398

Mark Strynar, Sonia Dagnino, Rebecca McMahan, Shuang Liang, Andrew Lindstrom, Erik Andersen, Larry McMillan, Michael Thurman, Imma Ferrer, and Carol Ball; "*Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS).*" *Environmental Science & Technology* 2015 49 (19), 11622-11630 DOI: 10.1021/acs.est.5b01215

Lasier, P. J., J. W. Washington, S. M. Hassan and T. M. Jenkins (2011). "*Perfluorinated chemicals in surface waters and sediments from northwest Georgia, USA, and their bioaccumulation in Lumbriculus variegatus.*" *Environmental Toxicology and Chemistry* **30**(10): 2194-2201.

Rankin, K., S. A. Mabury, T. M. Jenkins and J. W. Washington (2015). "*A North American and global survey of perfluoroalkyl substances in surface soils: Distribution patterns and mode of occurrence.*" *Chemosphere* **161**: 333-341.

Washington, J. W., J. J. Ellington, T. M. Jenkins and J. J. Evans (2007). "*Analysis of perfluorinated carboxylic acids in soils: Detection and quantitation issues at low concentrations.*" *Journal of Chromatography A* **1154**(1-2): 111-120.

Washington, J. W., W. M. Henderson, J. J. Ellington, T. M. Jenkins and J. J. Evans (2008). "*Analysis of perfluorinated carboxylic acids in soils II: Optimization of chromatography and extraction.*" *Journal of Chromatography A* **1181**(1-2): 21-32.

APPENDIX A

List of compounds, and mass thereof, to be spiked onto the XAD of each MM5 sample.

Compound	Abbreviation	Spike Amount
Perfluoro-n-[3,4,5- ¹³ C ₃]pentanoic acid	M3PFPeA	10 - 100 ng
Perfluoro-n-[1,2- ¹³ C ₂]decanoic acid	MPFDA	10 - 100 ng
Perfluoro-n-[1,2,3,4- ¹³ C ₄]octanoic acid	MPFOA	10 - 100 ng
Sodium perfluoro-1-[1,2,3,4- ¹³ C ₄]octanesulfonate	MPFOS	10 - 100 ng
2-Perfluorohexyl-[1,2- ¹³ C ₂]-ethanol (6:2)	M2FHET	10 - 100 ng
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)- ¹³ C ₃ -propanoic acid	M3HFPO-DA	10 - 100 ng